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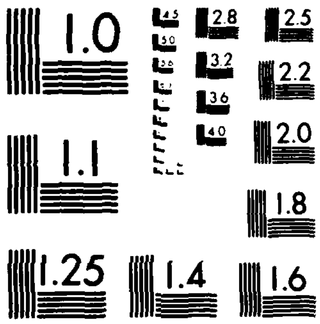

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By George O. Zimmerman

Principal Investigator

Physics Department

Boston University

Boston, MA 02215

Made to

Dr. M. Swerdlow

Building 410

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GRAPHITE INTERCALATED COMPOUNDS PROVED TO BE A PARTICULARLY FERTILE SYSTEM ON WHICH TO STUDY PHASE TRANSITIONS. IN THE CASE OF $FeCl_3$ INTERCALATED GRAPHITE AS WELL AS OTHER MAGNETIC INTERCALANTS, THE ROLE OF DIMENSIONALITY AS WELL AS THE IN-PLANE DENSITIES AND DEFECTS PLAY AN EXTREMELY IMPORTANT ROLE, AND ADD TO THE VARIETY OF CRITICAL PHENOMENA TO BE OBSERVED . THE INVESTIGATION SO FAR HAS YIELDED MANY INTERESTING RESULTS ON WELL CHARACTERIZED SAMPLES . WE HAVE STUDIED THE MAGNET PROPERTIES OF OUR SAMPLES AS A FUNCTION OF DEFECTS,

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ABSTRACT

Graphite intercalated compounds proved to be a particularly fertile system on which to study phase transitions[1]. In the case of $FeCl_3$ intercalated graphite as well as other magnetic intercalants, the role of dimensionality as well as the in-plane densities and defects play an extremely important role, and add to the variety of critical phenomena to be observed[2]. *The investigation so far* has yielded many interesting results on well characterized samples[3,4,5]. We have studied the magnet properties of our samples as a function of defects, probed by the Mössbauer technique, in-plane densities of the intercalant, and stage. Scientifically, the interest is in the nature of these transitions and their comparison to the various models such as the x-y model[6], the Potts model[7] and various other models, such as a spin glass, which predict anomalies in two dimensional systems which in the lower stages might become three dimensional in character. Author's Keywords

PROGRESS REPORT

As this investigation has shown[4], characterization is particularly important because samples prepared under identical conditions may have completely different structures and characteristics although their x-ray spectra were the same. In the compounds most thoroughly investigated by this group, $FeCl_3$ intercalated graphite, this investigation found that samples prepared under the same conditions may have different chemical compositions, $FeCl_2$ as well as $FeCl_3$. This was revealed by Mössbauer characterization. It is expected that in this investigation there will be enough correspondence between effects detectable by the Mössbauer effect, like the chemical composition and in-plane density, the number of vacancies related to the in-plane density, and others and the magnetic and electrical properties of the material so that the magnetic and electric properties themselves could be used to characterize a material. This would be particularly desirable for intercalants containing no isotopes suitable for Mössbauer analysis.

During the investigation of $FeCl_3$ intercalated graphite at this laboratory, several important discoveries were made about the electric and magnetic properties of these substances. It was found that in well characterized $FeCl_3$ samples there was a magnetic susceptibility maximum indicating a magnetic transition at 6.5 K in stage one and at 1.72 K in stage two[4]. At higher temperatures the magnetic susceptibility of these samples obeyed the Curie-Weiss law with the theta indicating an intiferromagnetic interaction within the layers and a ferromagnetic one between layers in stage one and antiferromagnetic interactions both within and between layers in stage two. Figure 1 shows the suceptibilities as a function of temperature while Figure 2 shows the inverse susceptibility and the Curie-Weiss law. Table 1 lists the various parameters for the transitions.

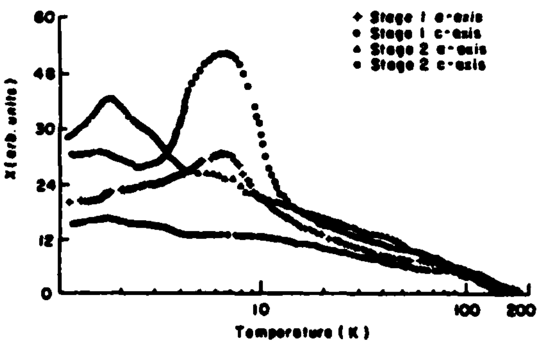

Figure 1. susceptibility (χ) versus temperature (T), plotted on a semi-logarithmic scale, for the stage 1 and 2 compounds. The measuring field was fixed both parallel (a-axis) and perpendicular (c-axis) to the basal plane. Notice the small amount of stage 1 (undetectable in the x-ray diffractograms) which can be detected in the stage 2 curve.

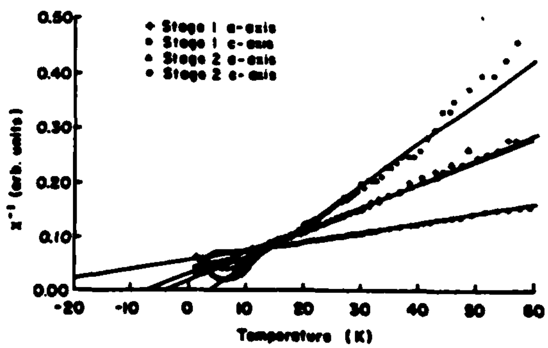

Figure 2. Inverse susceptibility (χ^{-1}) versus temperature (T) for the curves shown in Figure 1. The solid lines represent least squares fits to the data.

TABLE 1 This table lists the magnetic properties of the compounds.

STAGE	DIRECTION	TRANSITION TEMPERATURE	SUSCEPTIBILITY MAXIMUM	θ	CURIE CONSTANT (ARBITRARY UNITS)	NEAREST NEIGHBORS TO IRON VACANCIES
1	a-axis	4.3	6.5	-3.8	222	≤4%
1	c-axis	4.3	6.5	+3.8	132	≤4%
2	a-axis	1.3	1.72	-7.6	242	9%
2	c-axis	1.3	1.72	-33.0	575	9%

Possibly a more important discovery was that of a susceptibility maximum which occurs in $FeCl_3$ intercalated graphite at 1.7 K. That maximum occurs in each stage at the same temperature but its size becomes significantly greater with stage. Figure 3 shows this maximum in stage 1,2,4 and 6. The size of this maximum depends

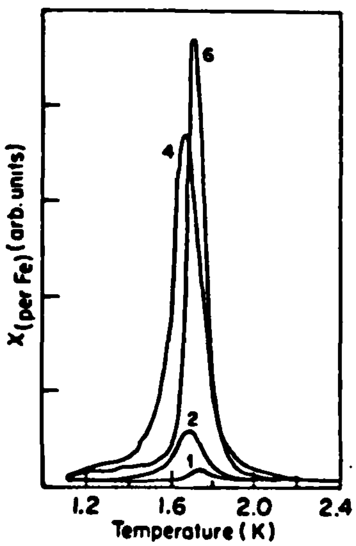

Figure 3. Measurements of susceptibility for magnetic fields perpendicular to the c-axis, $\chi_\perp$, vs temperature for graphite-$FeCl_3$ stages 1, 2, 4, and 6.

sensitively on the applied magnetic field. Figure 4 shows a trace of this maximum as a function of the liquid helium bath pressure, which is a monotonic function of temperature, in zero (higher peak) and the earth's magnetic field applied along the a-axis for a stage 6 sample.

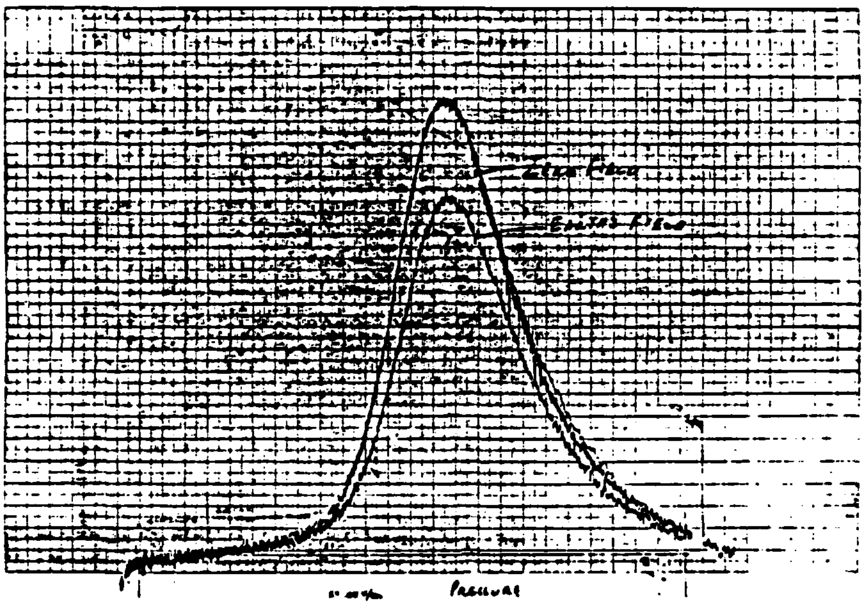

FIG. 4

Figure 5 shows the maximum in different magnetic fields applied along the c-axis while Figure 6 shows the field dependence along the a-axis.

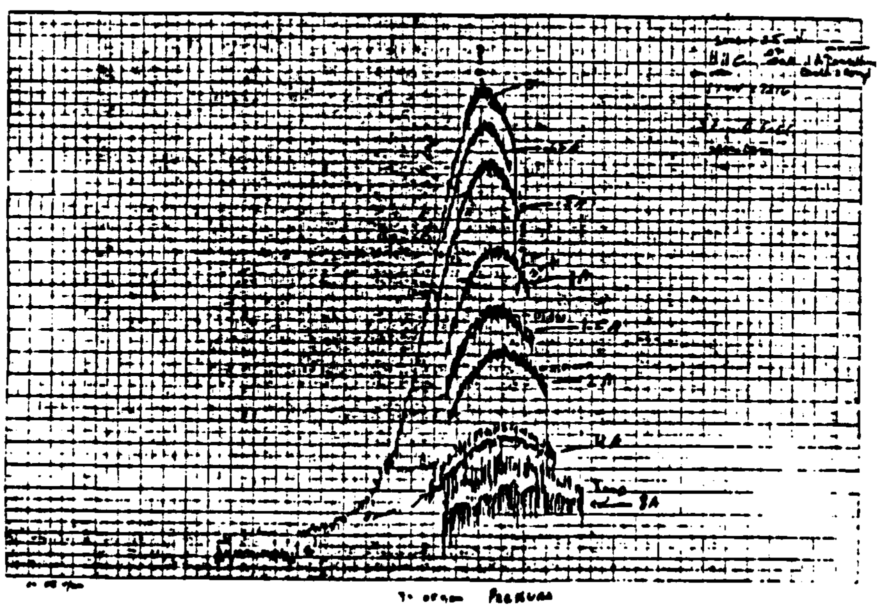

FIG. 5

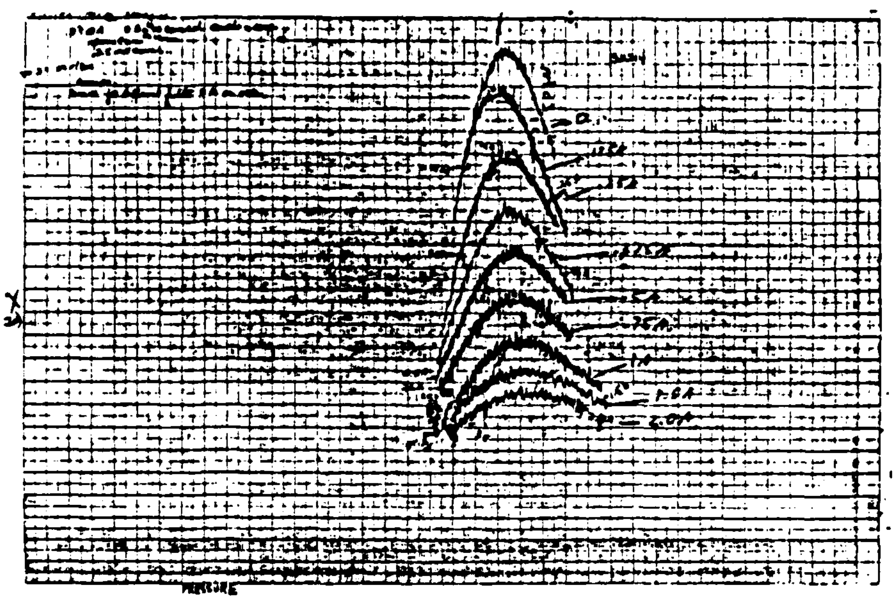

FIG. 6

The notations near the various traces indicate the current through the field coils with one ampere corresponding to 7 gauss. One notes that a field applied along the a-axis is much more effective in supressing the maximum than a field along the c-axis. The measuring field was always along the a-axis. Figures 7 and 8 show the field dependence of

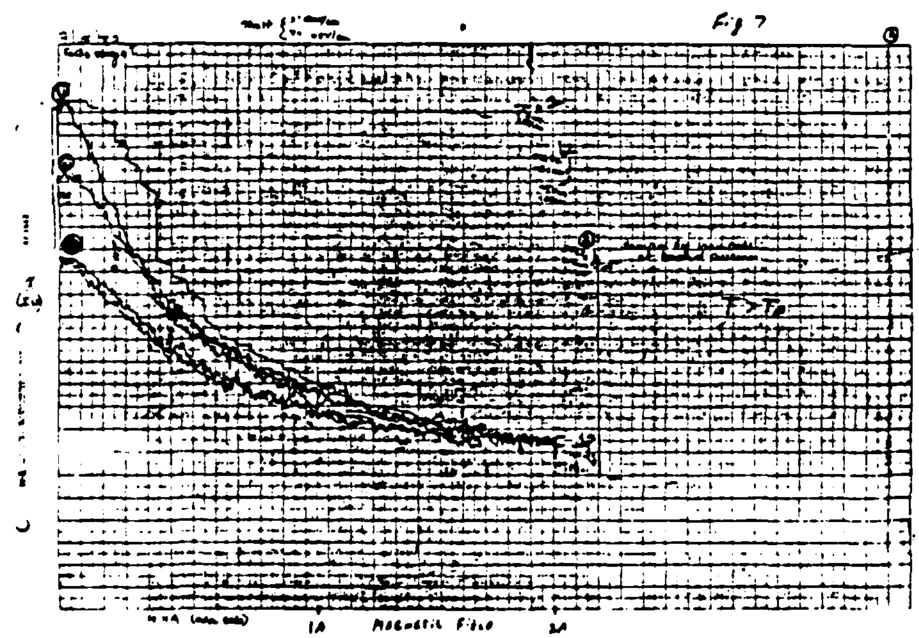

FIG. 7

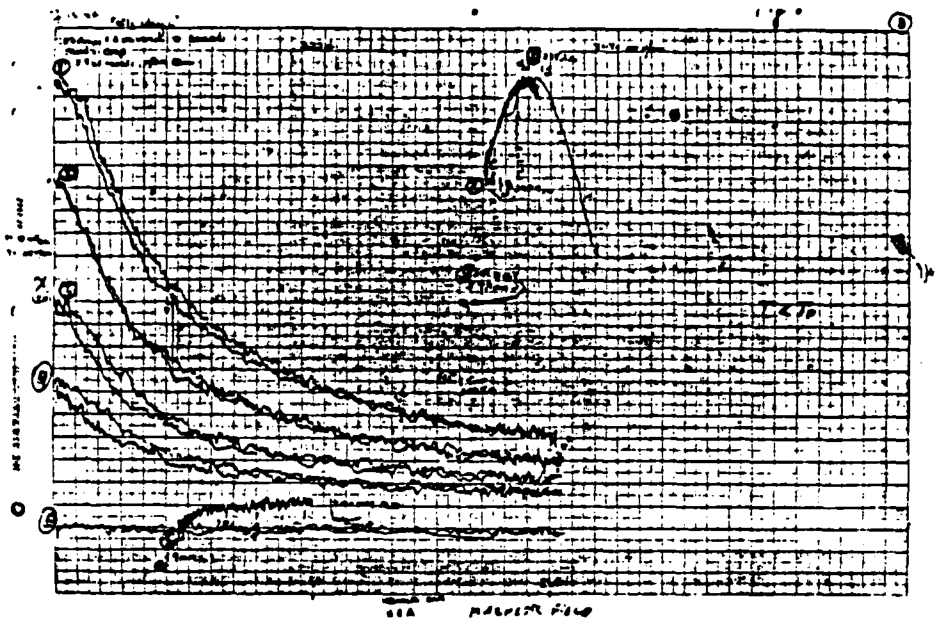

FIG. 8

the susceptibility at various temperatures above and below the maximum, with the field applied along the a-axis. Here the magnetic field is in units of current through the field coils (1A=7 gauss) and the numbers correspond to the susceptibility at zero field which could be correlated with the temperature of that particular isothermal sweep. Similar phenomena were found in $NiCl_2$ and $CoCl_2$ intercalated graphite[8]. By measuring the in-phase and out of phase components of the suscesptibility, one can infer that there is a resistivity maximum at the maximum in susceptibility. The in and out of phase (quad) susceptibilities of stage 6 are shown in Figure 9 while Figure 10 shows the conductivity as deduced from the phase shift.

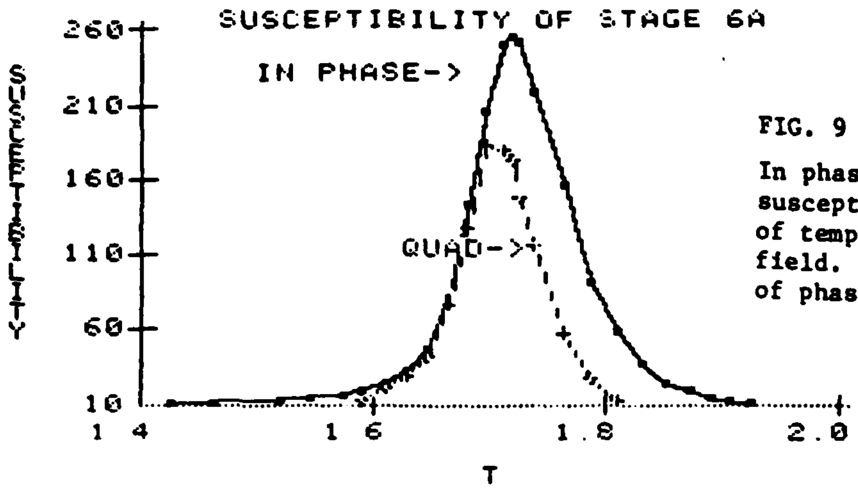

FIG. 9

In phase and out of phase susceptibility as a function of temperature in zero magnetic field. Quad denoting the out of phase component

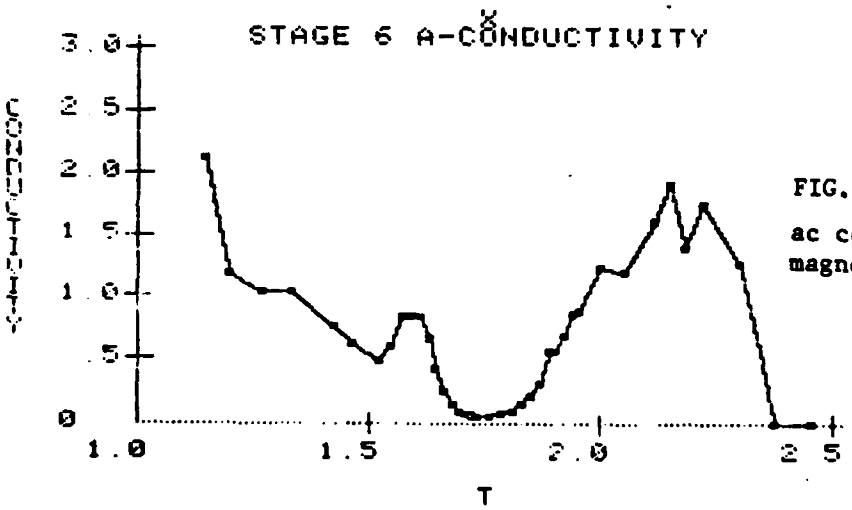

FIG. 10

ac conductivity in zero magnetic field

It was also shown that the size of the susceptibility maximum can be correlated, within a stage 2 sample, with the number of vacancies in that sample[5] as measured by the Mössbauer effect. This was shown for samples which have 7%,9% and 11% of their iron sites as nearest neighbors to iron vacancies. The susceptibilities as well as the Mössbauer spectra are shown in Figures 11 and 12. This, along with

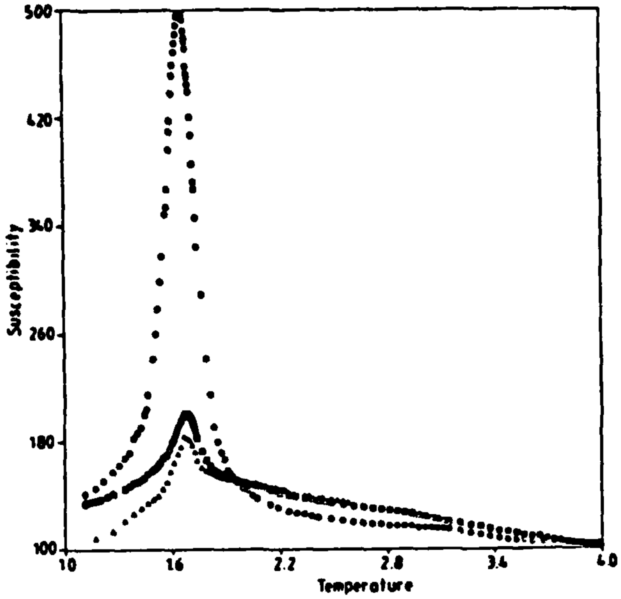

FIG. 11 Susceptibility versus temperature for three different stage 2 graphite–$FeCl_3$ compounds. The susceptibility is plotted in arbitrary units but each sample has been normalised for the relative amount of iron it contains. △, sample 1; □, sample 2; ○, sample 3.

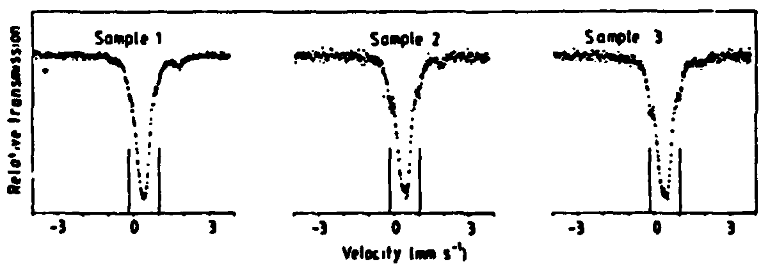

FIG. 12 Corresponding Mössbauer spectra for the three samples whose susceptibility curves are shown in *figure 1*. *The position of the two peaks which comprise the iron sites nearest* neighbour to iron vacancies are indicated by the straight lines. Zero velocity is measured *relative to the centre of gravity of an iron foil spectrum at room temperature.*

the power dependence of the susceptibility peak, corrected for the shape factor, at temperatures above the maximum, argues strongly that the maximum is an indication of a spin glass[7a] transition. Figure 13 shows the log

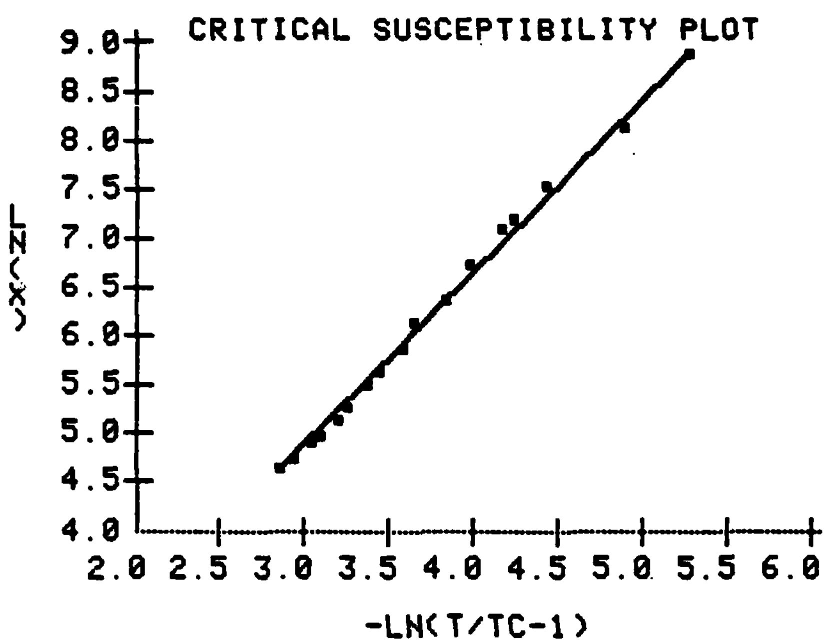

FIG. 13

of the susceptibility plotted against the log of the reduced temperature (T/Tc-1) for zero applied field. It was also shown[9] that the in-plane density of $FeCl_3$ decreases with the stage which may explain the variation of the size of the susceptibility maxium with stage. The in-plane density dependence on staging is corroborated by the theoretical investigation of the structure of graphite intercalated systems by Millman and Kirzcenow[10] at Boston University.

PUBLICATIONS which were partially supported by this grant are:

a) S.E. Millman and G.O. Zimmerman "Observation of Spin Glass State In $FeCl_3$: Intercalated Graphite," Journal of Physics C16, 189 (1983).

b) S.E. Millman, "Microscopic Analysis of Stage Dependent Intercalant In-Plane Density in Graphite $FeCl_3$," Physics Letters 92A, 441, (1982).

c) G.O. Zimmerman, D. Solenberger and D. Gata "Critical Behavior of the 1.7 K Transition in $FeCl_3$ Intercalated Graphite" in preparation.

*d) S.E. Millman, B.W. Holmes and G.O. Zimmerman, Solid State Communications 43, 903 (1982).

*e) M. Elahy, C. Nicolini, G. Dresselhaus and G.O. Zimmerman, Solid State Communications 41, 289 (1982).

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*h) S.E. Millman, Ph.D Dissertation, "Magnetic, Electronic and Structural Properties of $FeCl_3$ Intercalated Graphite", Boston University (1982).

PERSONS ASSOCIATED WITH THIS GRANT:

G.O. Zimmerman, Principal Investigator, Professor

C. Nicolini, Research Associate

S.E. Millman, Research Assistant, Graduate Student, Ph.D. 1982 (Boston University)

D. Solenberger, Graduate Student

D. Gata, Graduate Student

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